

STABILITY AND PHOTOCHEMISTRY OF ClO DIMERS FORMED
AT LOW TEMPERATURE IN THE GAS PHASE

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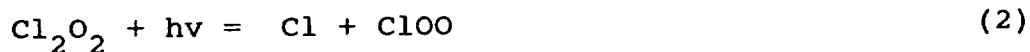
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Abstract

The recent observations of elevated concentrations of the ClO radical in the austral spring over Antarctica have implicated catalytic destruction by chlorine in the large depletions seen in the total ozone column. One of the chemical theories consistent with an elevated concentration of the ClO is a catalytic cycle involving the formation of the ClO dimer through the association reaction:



and the photolysis of the dimer to give the active Cl species necessary for O_3 depletion.



In the present paper we report experimental studies designed to characterise the dimer of ClO formed by the association reaction (1) at low temperatures. ClO was produced by static photolysis of several different precursor systems: $\text{Cl}_2 + \text{O}_3$; $\text{Cl}_2 + \text{Cl}_2\text{O}$; $\text{OClO} + \text{Cl}_2\text{O}$, O_2 or N_2 . The reaction products were investigated by photodiode array spectroscopy in the U.V. region, which allowed the time dependence of Cl_2 , Cl_2O , ClO, OClO, O_3 and other absorbing molecules to be determined.

Fig. 1 shows product spectra recorded in three different ClO precursor systems at 233K. Spectra 1a and 1b were obtained using the reactions of $\text{Cl} + \text{O}_3$ and $\text{Cl} + \text{Cl}_2\text{O}$ as a source of ClO. These appear to be associated with the major product of the $\text{ClO} + \text{ClO}$ reaction in the temperature range 200-273K, which we believe to be the dimer Cl_2O_2 . The absorption scales with $[\text{ClO}]^2$ and becomes more stable as temperature decreases. By means of mass balance a value of $(6.4 \pm 0.6) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ was obtained for the cross-section at the peak of absorption at 245 nm. By observation of the temperature dependence of the concentration ratio $[\text{Cl}_2\text{O}_2]/[\text{ClO}]^2$, an expression is obtained for the equilibrium constant for reaction (1):

$$K_1 = (4.2 \pm 0.3) \times 10^{-30} \cdot T \cdot \exp(8720 \pm 360)/T \text{ cm}^3 \text{ molecule}^{-1}$$

Fig. 2 shows a Van't Hoff plot of the resultant values of K which

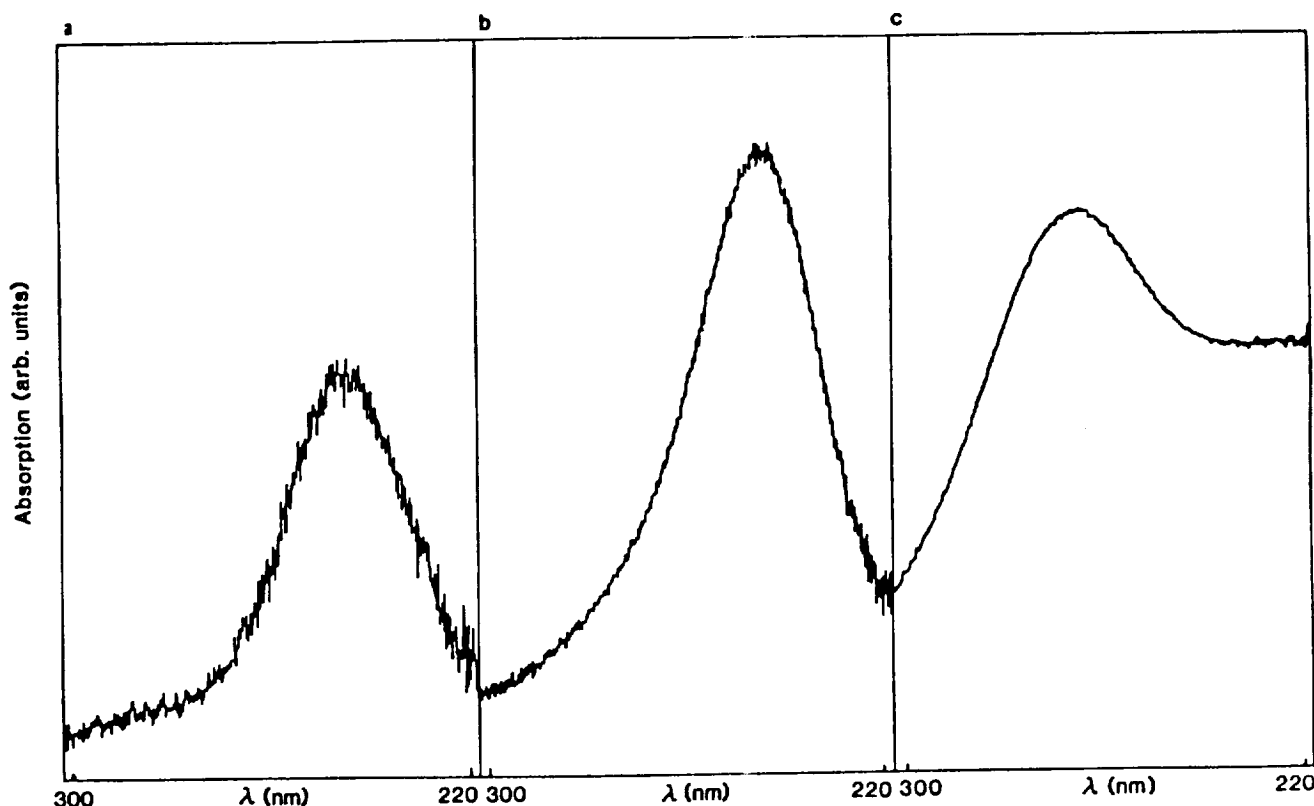


Fig. 1 - Residual absorptions seen in the photolysis of (a) $\text{Cl}_2/\text{O}_3/\text{N}_2$ mixtures (b) $\text{Cl}_2/\text{Cl}_2\text{O}/\text{N}_2$ mixtures (c) $\text{OClo}/\text{Cl}_2\text{O}/\text{N}_2$ mixtures

allow determination of $\Delta H_1 = -72.5 \pm 3.0 \text{ kJ mol}^{-1}$ and $\Delta S_1 = -144 \pm 11 \text{ J mol}^{-1} \text{ K}^{-1}$

The third spectrum in Fig. 1 was obtained when the photolysis of a $\text{OClo} - \text{Cl}_2\text{O} - \text{N}_2$ mixture was used to make ClO :



The spectrum, which could also be produced in $\text{OClo} - \text{O}_2$ and $\text{OClo} - \text{N}_2$ photolysis systems at low temperature, differs significantly from that obtained in the systems without OClo present. At higher temperatures and longer reaction times the spectrum changed shape to give an absorption bearing a strong resemblance to that assigned to Cl_2O_2 . The absorbance at short reaction times scaled approximately with the product $[\text{OClo}] \times [\text{ClO}]$ indicating the formation of an adduct, Cl_2O_3 , via reaction of OClo with ClO . The Van't Hoff plot of the equilibrium



constants calculated on this basis at three temperatures in the range

233-273K is shown in Fig. 2.

The following thermochemical quantities were derived for reaction (6):

$$\Delta H_6 = -68.1 \pm 2.6 \text{ kJ mol}^{-1} ; \Delta S_6 = -165 \pm 10 \text{ kJ.mol}^{-1}\text{K}^{-1}$$

We have also made a preliminary investigation of the photolysis of the Cl_2O_2 dimer, using light at 254 nm, close to the absorption maximum.² Our results indicate that the major photolysis channel is reaction (2) producing a Cl atom and a ClOO peroxy radical, as suggested for the proposed catalytic cycle for O_3 removal in the antarctic stratosphere. This suggests that the 'stable' form of Cl_2O_2 that we observe is of a peroxy type structure: Cl-O-O-Cl. This is consistent with theoretical calculations of the geometry and structure of the possible ClO dimers.

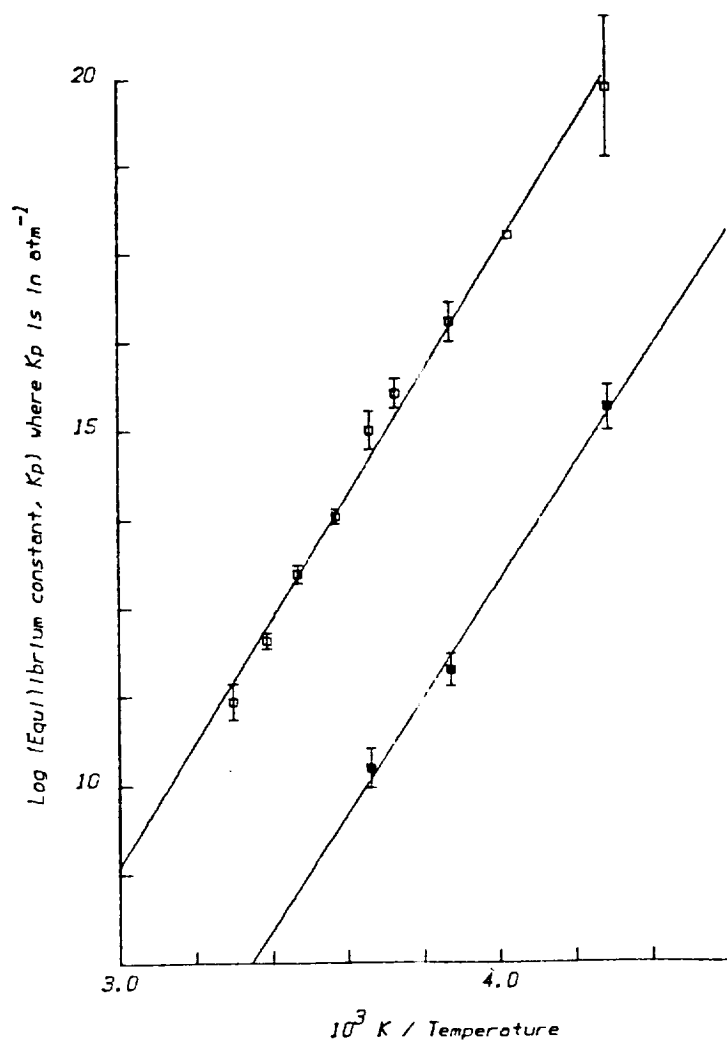


Fig. 2 - A Van't Hoff plot of $\log_e K_p$ against T^{-1} for the equilibria: $\text{ClO} + \text{ClO} = \text{Cl}_2\text{O}_2$ (upper plot) and $\text{ClO} + \text{OCLO} = \text{Cl}_2\text{O}_3$ (lower plot).